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Original article

Effect of labyrinth-like arrays formation of nickel nanorods on nickel surface as a result of galvanic substitution reaction in aqueous solutions of $CuCl_2$ and NaCl mixture

Valeri P. Tolstoy[a], Kirill D. Nikitin[b], Elisaveta V. Batischeva[c]

Institute of Chemistry, St. Petersburg State University, St. Petersburg, Russia

[a]v.tolstoy@spbu.ru, [b]st069423@student.spbu.ru, [c]batischevaelisaveta@gmail.com

Corresponding author: Valeri P. Tolstoy, v.tolstoy@spbu.ru

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ABSTRACT The article describes the nickel surface treatment conditions in aqueous solutions of a mixture of $CuCl_2$ and NaCl salts. This investigation reveals the occurrence of selective etching on the nickel surface, facilitated by a galvanic replacement reaction (GRR). The etching process gives rise to the formation of arrays of labyrinths with walls of nickel nanorods with a diameter ranging from 10 to 50 nanometers and a length of up to 0.5 micrometers are formed, located primarily in the direction perpendicular to the surface. The experimental results obtained have enabled the formulation of hypotheses concerning the sequence of chemical reactions occurring on the surface and the role of the A. Turing diffusion-chemical model in the formation of the observed labyrinths. It has been demonstrated that the presence of such labyrinths on the surface of nickel leads to a decrease in the angles of its wetting with water.

KEYWORDS nickel, $CuCl_2$, galvanic replacement, nanorods, arrays

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1. Introduction

Galvanic replacement reactions of atoms on the surface of nickel are carried out by processing it in aqueous solutions of salts or complex compounds of more noble metals, and this makes it possible to obtain a fairly wide range of practically important nanoscale particles on its surface, including Au(0) [1], Pd(0) [2], Pt(0) [3–5], and a number of their alloys [6]. In such reactions, a salt or a complex compound of a more noble metal plays a role of an oxidiser of Ni(0) atoms on the surface. This process leads to the transition of nickel cations into solution and the formation of noble metal nanoparticles with different morphologies on the surface.

Among such reactions, the galvanic replacement reaction in $CuCl_2$ solutions is of particular importance. This reaction has been repeatedly used to create a layer of CuCl [7] nanoparticles on the nickel surface or to dissolve nickel particles in various composite ceramics [8]. A discussion of the features of this reaction on the nickel surface inevitably gives rise to consideration of the results that were previously obtained during the treatment of the surface and other metals with a solution of this salt. In particular, a mixture of $CuCl_2$ and NaCl solutions in [9] and [10] was used to dissolve Pd or Pd and Ag, respectively, on the surface of waste printed circuit boards.

In these articles, the selection of aqueous solutions of a mixture of $CuCl_2$ and NaCl salts was due to the fact that in these solutions, at the initial stage of the reaction, a galvanic replacement reaction occurs on the surface of the marked metals and Cu(0) nanocrystals are formed, which then react with an excess of $CuCl_2$ and form CuCl nanocrystals. In turn, the latter, dissolve in excess of NaCl to form a complex compound $CuCl_2^-$ in solution. In this case, the conditions of these reactions were primarily selected with the objective of resolving the issues associated with hydrometallurgy, i.e., the complete dissolution of crystals of these metals and their transfer to solutions resulting in the formation of corresponding salts.

The aim of this work was to research the features of selective etching of the nickel surface in aqueous solutions of $CuCl_2$, during which various types of ”patterns” were formed on it.

2. Experiment

GRRs were carried out on the surface of NP-2 nickel foil, which had been cut into plates with dimensions of approximately $15\times10\times0.05$ mm. The processing of such foil was carried out in aqueous solutions of $CuCl_2{\cdot}2H_2O$, NaCl and HCl, which were produced by JSC "Nevareactive" and their degree of purity corresponded to "analytical grade reagent". In order to prepare the reagent solutions, the salt samples were dissolved in deionised water with continuous stirring on a magnetic stirrer. The interval between the preparation of the solution and its subsequent application was at least a day.

To remove organic contaminants, the initial nickel foil samples were processed 2 times in isopropyl alcohol for 10 minutes in an ultrasonic bath with a generator power of 50 watts and an operating frequency of 35 kHz. Then they were etched in a 3 M aqueous HCl solution for 30 minutes at a temperature of 60 °C also in an ultrasonic bath and then washed 3 times with deionised water and dried in air.

In the course of the research, the characteristics of the GRR on the nickel surface in aqueous solutions of $CuCl_2$ and a mixture of $CuCl_2$ and NaCl were studied. The copper salt concentration was set at 0.2 increments in the range of 0.2 – 1.0 m, and the NaCl concentration was set at 0.5 increments in the range of 0.5 – 5 m. The duration of each treatment ranged from 5 minutes to 2 hours or more. To study the effect of the composition of the gaseous atmosphere on the processes on the surface of nickel, a number of experiments were conducted not only in the atmosphere of air, but also oxygen and argon. The solutions were pre-saturated with the appropriate gases by passing them through the solutions for 20 minutes. The surface treatment of the samples with all solutions was carried out at room temperature and atmospheric pressure.

In the course of the study, the orientation of crystals on the nickel surface was determined by means of an Oxford Instruments Electron Backscattered Diffraction (EBSD) system when the samples were observed under a Zeiss Merlin electron microscope. The composition of compounds on the nickel surface was determined by Electron Microprobe Analysis (EMPA) using an Oxford INCA-350 EDX spectrometer when the samples were observed under a Zeiss EVO40EP microscope. The wetting angles were measured using an Open Science goniometer equipped with a ToupCam digital camera. For this purpose, 1 μl of deionized water was applied to the sample surface from a distance of 2 mm using a Thermo Scientific Light microdoser. For each sample, the angles were measured at 3 to 4 points on its surface.

3. Results and discussion

At the first stage of the work, the effect of salt concentration in solutions of a mixture of $CaCl_2$ and NaCl on the formation of ordered structures on the nickel surface was studied. In order to achieve this, a series of samples were obtained through nickel processing for 1 hour. The study of the surface morphology of such samples by the SEM method showed that at concentrations of $CuCl_2$ in the range of 0.4 – 1.0 m and NaCl concentrations of 2.5 – 5.0 m, etching pits with walls arranged in the form of peculiar labyrinths can be observed on the surface. Moreover, the effect of the formation of such labyrinths is most pronounced after treatment in a solution of a mixture of salts with a concentration of $CuCl_2$ equal to 1.0 m and NaCl equal to 5.0 m. Subsequently, the effect of processing time on the formation of these structures was analysed for this mixture of salts. The analysis of the nickel surface by SEM of a series of such samples allowed us to identify the main stages of the process.

As demonstrated in the micrographs shown in Fig. 1, the GRR proceeds locally at the first stages, resulting in the formation of individual depressions with a diameter of several tens of nanometers on the surface (Fig. 1a). Over time, the size of these depressions increases and new ones are formed (Fig. 1b). These depressions gradually evolve into a discernible "pattern" on the surface. It is our contention that this "pattern" is primarily attributable to the dimensions of nickel polycrystals. The process of depression widening gives rise to the formation of a groove-like structure on the surface. Arrays of grooves form more pronounced patterns, visually resembling mazes (Fig. 1b). Then the grooves in these labyrinths deepen and widen (Fig. 1c,d). Further widening of the grooves leads to a decrease in the thickness of the walls between them. Consequently, as shown in Fig. 2 micrographs, several solid groove wall transforms into a set of individual nanorods with a diameter of approximately 10 – 50 nm and a length of up to 0.5 microns, oriented mainly along the normal to the surface. Nickel surface treatment in a similar solution for 3, 5, and 7 hours showed that a proportion of the nanorods dissolved and the pattern of the labyrinths became less pronounced (these micrographs are not shown in Figs. 1, 2).

As demonstrated by the experimental findings, the formation of such labyrinths is influenced by oxygen dissolved in a mixture of these salts. Fig. 3 shows a change in the morphology of the labyrinths with a change in the concentration of O_2 in solution. When O_2 is completely removed using Ar (Fig. 3a,d), the depth of resultant labyrinths exhibit a reduced depth when compared to those formed under the conditions of the reaction is carried out in an air atmosphere (Fig. 3b,e). When using a solution that is saturated with O_2, during the same treatment time, the walls of the labyrinths actually collapse and arrays of Ni nanorods oriented normally to it form on the nickel surface (Fig. 3b). From the results presented, we are able to conclude that the presence of O_2 accelerates the reaction of anisotropic nickel etching under the conditions of the GRR.

Examination of the Ni surface after treatment in a solution of a mixture of $CuCl_2$ ($C = 1$ m) and NaCl ($C = 5$ m) salts for two hours using the EBSD method showed that the vertices of the maze walls represent the faces of a Ni crystal with a crystallographic index $\{110\}$ (Fig. 3). Accordingly, anisotropic etching occurs mainly perpendicular to this and its

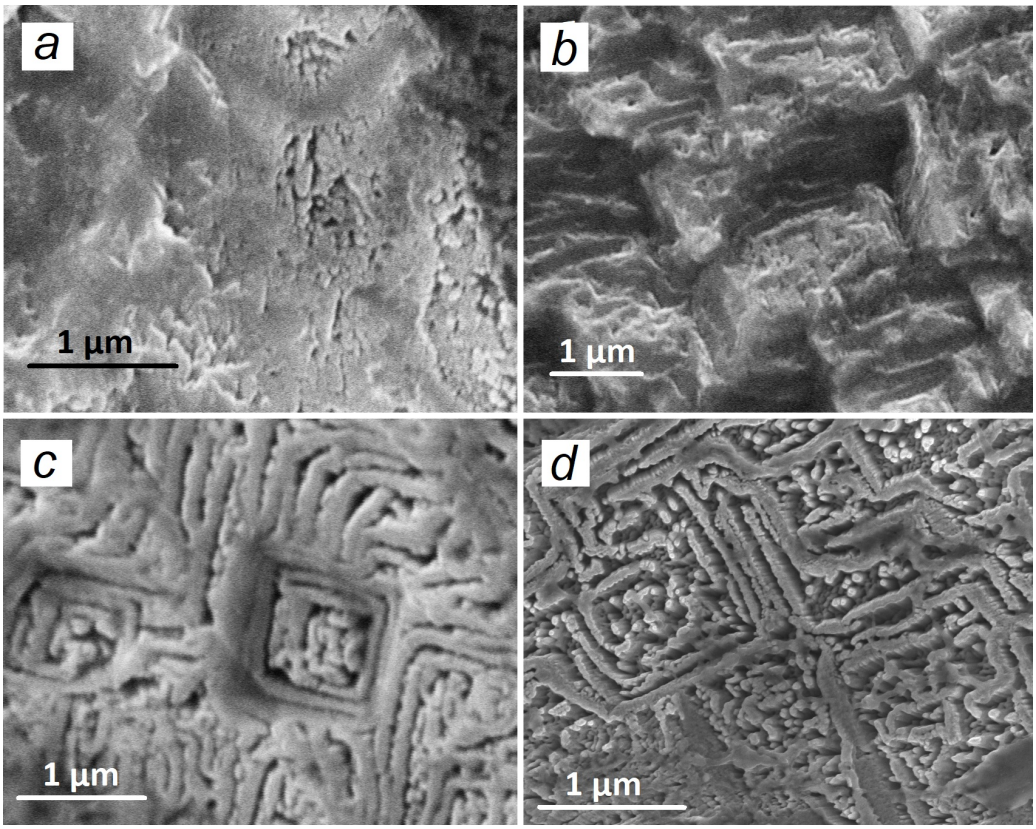

FIG. 1. SEM images of the nickel surface after treatment in a solution of a mixture of $CuCl_2$ ($C = 1$ m) and NaCl ($C = 5$ m) salts for (a) 5 minutes, (b) 15 minutes, (c) 30 minutes, (d) 2 hours. The images are obtained by observing from above

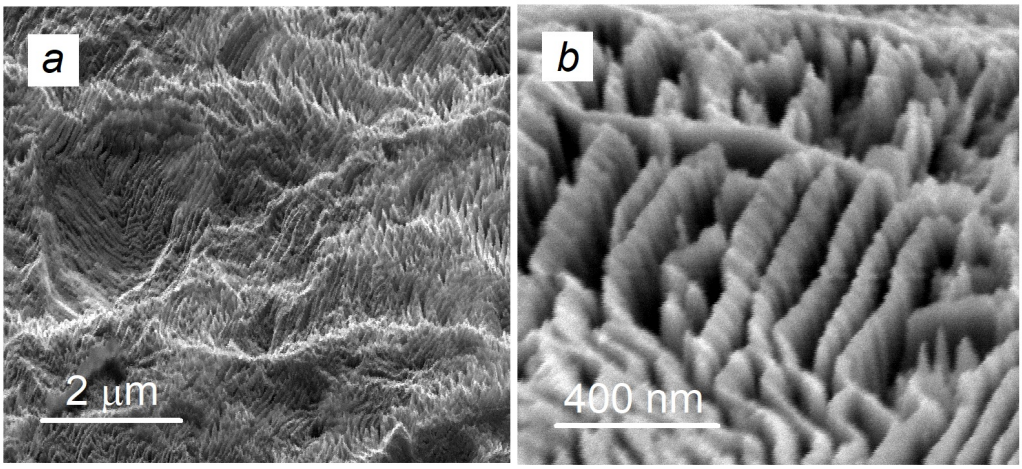

FIG. 2. SEM images of the nickel surface after treatment in a solution of a mixture of $CuCl_2$ ($C = 1$ m) and NaCl ($C = 5$ m) salts for 2 hours. The images were obtained when viewed at an angle of 45°

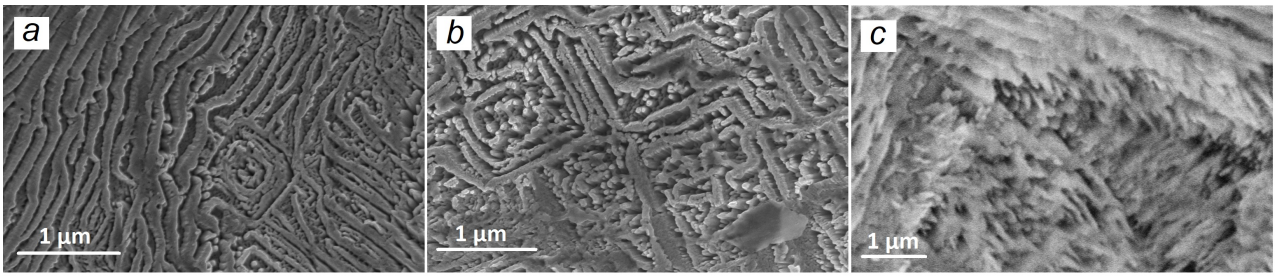

FIG. 3. SEM images of the nickel surface after treatment for 2 hours in a solution of a mixture of $CuCl_2$ ($C = 1$ m) and NaCl ($C = 5$ m) salts. (a) – treatment in an Ar atmosphere; (b) – treatment in an air atmosphere; (c) – treatment in an O_2 atmosphere

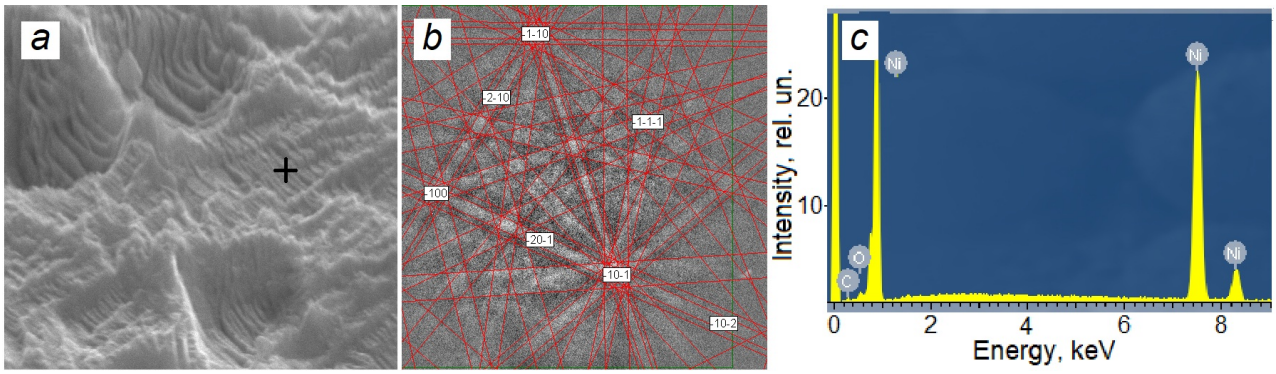

FIG. 4. SEM micrography (a) of the nickel surface after treatment for 2 hours in a solution of a mixture of $CuCl_2$ ($C = 1$ m) and NaCl ($C = 5$ m) salts and a diffraction pattern of backscattered electrons (b), which was obtained at the point indicated by the crosshair in Fig. 4a

equivalent faces. It is important that the results of the EMPA indicate the absence of copper, sodium and chlorine atoms on the surface, which could remain on the surface of the sample treatment field in a solution of a mixture of the marked salts taken in such a high concentration (Fig. 4d).

Based on the above facts, the following model of the processes occurring on the surface of Ni during its treatment in a solution of a mixture of $CuCl_2$ and NaCl salts can be proposed. Thus, at the first stage of the GRR Cu(0) nanoparticles are formed on the nickel surface (1). These nanoparticles subsequently react with Cu^{2+} ions from solution, resulting in the formation of a difficult-to-dissolve CuCl precipitate on the surface (2). It blocks the access of Cu^{2+} ions to Ni(0), which slows down the GRR and, consequently, the further formation of CuCl.

$$Ni(0) + CuCl_2 \rightarrow NiCl_2 + Cu(0), \quad (1)$$

$$Cu(0) + CuCl_2 \rightarrow 2CuCl. \quad (2)$$

Concurrently, the CuCl precipitate is dissolved in an excess of chloride ions by reaction (3) thereby releasing the Ni(0) surface is for further GRR, resulting in accelerated formation of new Cu(0) nanoparticles:

$$CuCl + Cl^- \rightarrow [CuCl_2]^-. \quad (3)$$

Along with the formation of $[CuCl_2]^-$, the formation of $[CuCl_3]^{2-}$ can also be observed in solution (Fig. 5a).

In addition, it was observed that with increasing treatment time in a solution of a mixture of salts, its pH increases from an initial value of 2.1 to 4.1 after the reaction has been carried out for 2 hours. This leads to the formation of a difficult-to-dissolve compound $CuCl_2 \cdot 3Cu(OH)_2$ by reaction (4), which exists in solutions with pH values in the range of 3 – 8 as illustrated in Fig. 5a. Furthermore, this compound is apparently deposited mainly on the nickel surface, as a local pH increase occurs there.

$$4CuCl_2 + 6OH^- \rightarrow CuCl_2 \cdot 3Cu(OH)_2 + 6Cl^-. \quad (4)$$

Thus, several successive and competing reactions occur in the system. Reaction (2) slows down reaction (1). Concurrently, reaction (3) accelerates reaction (1) by freeing the surface of Ni(0) from the presence of insoluble compounds. In turn, reaction (4) slows down reactions (1–3). The state of such a system is controlled by the ratio of the rates of chemical reactions and ion diffusion, which change dynamically. Such systems are referred to as reaction-diffusion or A. Turing systems in the literature, and are currently under active study, as they provide a unique approach to the self-assembly of nano- and micro-dimensional structures [12–14]. Such systems have been demonstrated to be responsible, for example,

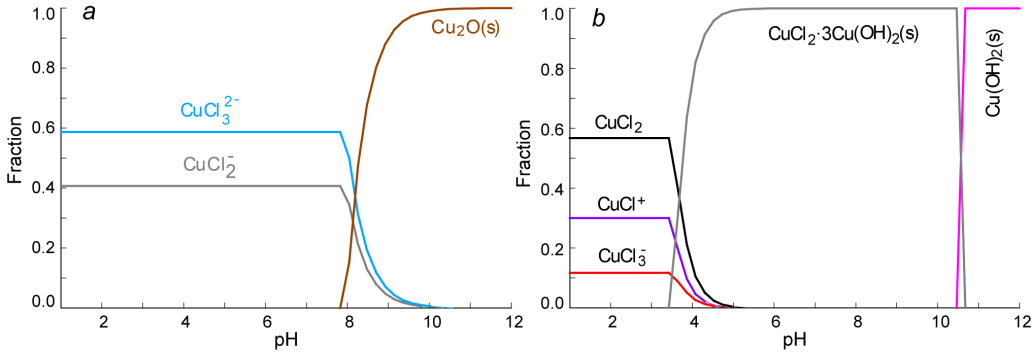

FIG. 5. The change in the calculated values of the mole fractions of various complex compounds in solutions of mixtures of CuCl and NaCl (a) and $CuCl_2$ and NaCl (b) salts, depending on the pH values. The calculations were performed using the Hydra-Medusa hydrochemical equilibrium modeling program [11]

for the formation of patterns on the skin of animals during their growth [15–19]. In addition, when interpreting these results, it should be borne in mind that GRR occurs inside the grooves at the stage of pattern formation, which means that self-organisation in the system is observed under conditions of spatial constraints, which, as is known [20], contribute to the morphology of reaction products.

As already noted, the transition of the complex compound $[CuCl_2]^-$ from the nickel surface to the solution is a relatively slow process. In our opinion, the process of oxidation of Cu(I) cations to the degree of Cu(II) can play a role in the dissolution process, which is realised, for example, by reaction (5). As demonstrated in Fig. 5b, at the equilibrium pH of the mixed salt solution, Cu(II) cations easily dissolve in the presence of excess chloride ions (reaction 6):

$$CuCl + O_2 + 2H_2O \rightarrow 4CuOHCl, \quad (5)$$

$$Cu(OH)Cl + 2Cl^- \rightarrow [CuCl_3]^- + OH^-. \quad (6)$$

As shown in Fig. 3, the presence of oxygen molecules in the solution accelerates the GRR reaction. This experimental result appears to provide confirmation of the considered model of the sequence of chemical reactions on the nickel surface under GRR conditions.

In a series of experiments, it was also found that when Ni is treated in a solution of a mixture of $CuCl_2$ and NaCl, its surface acquires a greater degree of hydrophilicity than that of the original nickel surface. Furthermore, it was determined that this degree increases with increasing treatment time in soluti from 1 to 2 hours. As illustrated in Fig. 6, the angle of wetting nickel with water was measured in a series of several samples. It was found that the maximum treatment time in a solution of a mixture of salts resulted in a 20° decrease in the edge angle of wetting the surface with water in comparison with the untreated surface of nickel. This effect is purportedly attributable to a distinctive "flow" of water into the grooves of the maze. These results, therefore, indicate the possibility of a controlled change in the wetting angles of the nickel surface in a relatively simple way by treating it in a solution of a mixture of salts.

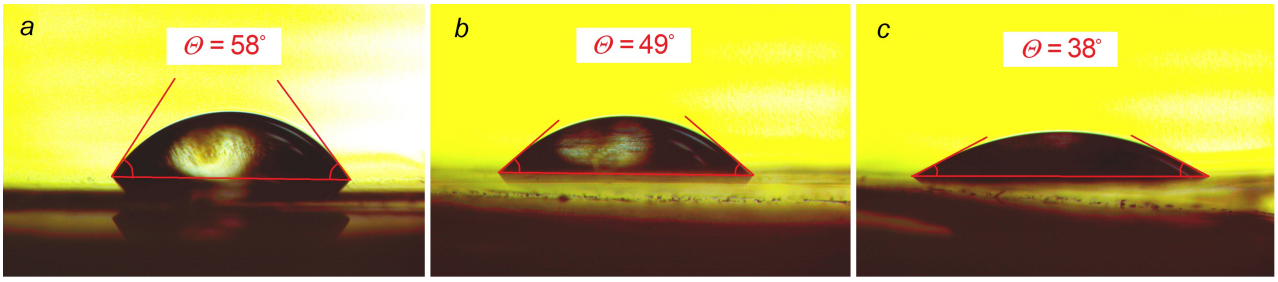

FIG. 6. The angles of wetting the nickel surface with water. (a) – before the measurement, the nickel is treated in HCl solution; (b) – treated in a solution of a mixture of $CuCl_2$ (1 m) and NaCl (5 m) for 1 hour; (c) – treated in a solution of a mixture of $CuCl_2$ (1 m) and NaCl (5 m) for 2 hours

4. Conclusion

A research of the features of nickel surface treatment in solutions of a mixture of $CuCl_2$ and NaCl salts showed that the effect of etching pits on its surface in the form of labyrinths with walls of nickel nanorods is most pronounced at a concentration of $CuCl_2$ equal to 1 m and NaCl concentration equal to 5 m with a treatment time of 2 hours. An increase in the reaction rate of GRR and the depth of the labyrinths was demonstrated with an increase in the concentration of oxygen dissolved in the mixture of the indicated salts. It is shown that the treatment of nickel in a solution of such salts leads to an increase in the degree of hydrophilicity of its surface.

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Information about the authors:

Valeri P. Tolstoy – Institute of Chemistry, Saint Petersburg State University, University St. 26, Peterhof, Saint Petersburg, 198504, Russia; ORCID 0000-0003-3857-7238; v.tolstoy@spbu.ru

Kirill D. Nikitin – Institute of Chemistry, Saint Petersburg State University, University St. 26, Peterhof, Saint Petersburg, 198504, Russia; ORCID 0009-0007-1409-5214; st069423@student.spbu.ru

Elisaveta V. Batischeva – Institute of Chemistry, Saint Petersburg State University, University St. 26, Peterhof, Saint Petersburg, 198504, Russia; ORCID 0000-0001-8264-2135; batischevaelisaveta@gmail.com

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